

Anthropogenic and Natural Constituents in PM10 at Urban and Rural Sites in North- Western Europe: Concentrations, Chemical Composition and Sources

Ernie Weijers and Martijn Schaap

Abstract This study focuses on north-western region of Europe discussing questions like the following: Which anthropogenic and natural constituents build up the particulate matter? To what extent do they contribute to the total mass? And where do these constituents originate? To answer, we elaborated data sets containing chemical information of PM recently becoming available in the Netherlands, Germany and Belgium.

The chemical composition of PM10 shows a considerable conformity in these countries. Always, secondary inorganic aerosols (SIA) are the major constituent ($\pm 40\%$) followed by the carbonaceous compounds ($\pm 25\%$). Contributions of sea salt and mineral dust vary between 10% and 15% depending on presence and distance of respective sources. The unidentified mass is some 15% indicating that the composition of PM10 in this region is fairly well known.

PM10 concentrations and constituents appear systematically higher at urban sites. Urban increments have been measured for most chemical constituents. Nearby (anthropogenic) sources and reduced dispersion in the urbanised areas are the main determining factors here. The observed increment for SIA is caused by more nitrate and sulphate. It is explained by depletion of chloride stabilising part of the nitrate and sulphate in the coarse mode. The question then arises how to assign the coarse mode nitrate (and sulphate) in the mass closure exercise as they replace the chloride.

Important for the national and European air pollution policy is how much of the measured particulate matter is of anthropogenic origin. A simple assessment indicates that 20–25% of PM10 is of natural origin; hence, the majority of PM10 in the north-western-European region is of anthropogenic origin. The uncertainty in this analysis is considerable, and the result is indicative.

E. Weijers (✉)

Energy research Centre of the Netherlands (ECN), P.O. Box 1, 1755 ZG Petten, The Netherlands
e-mail: weijers@ecn.nl

M. Schaap

TNO, P.O. Box 80015, 3508 TA Utrecht, The Netherlands

30 A chemical transport model (LOTOS-EUROS) was used to obtain a detailed
 31 source apportionment. In total, 75% of the modelled PM10 mass could be explained.
 32 The important contributions to PM10 come from agriculture, on- and off-road
 33 transport and natural sources (sea salt). Secondary contributions are derived from
 34 power generation, industrial processes and combustion as well as households. Of the
 35 modelled part, 70–80% of PM10 over the Netherlands is anthropogenic. The
 36 increase in source contribution going from low to high PM levels is proportional
 37 for most sectors, except for agriculture and transport, which become more important
 38 mainly due to the more than proportional rise in ammonium nitrate concentrations.
 39 Sea-salt concentrations decline with rising PM10. The same was found for Spain, but
 40 here, the impact of Saharan dust on PM episodes is clearly recognisable and much
 41 larger than in north-western Europe. Natural sources in Spain contribute about half
 42 of the modelled PM10 concentrations. Significant anthropogenic sources are similar
 43 to those in north-western Europe.

44 **Keywords** Anthropogenic contribution, Chemical composition, Chemical trans-
 45 port modelling, Natural contribution, North-western Europe, PM10, Source appor-
 46 tionment, Spain

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58 1 Introduction and Scope

59 Although air quality in Europe has improved substantially over the last decades, it
 60 still poses a significant threat to human health [1]. Short- and long-term health
 61 effects have been described, but so far there is no conclusive evidence which
 62 component(s) or property can be held responsible. As a consequence, the European
 63 air quality guidelines keep a focus on particulate mass, and, next to the PM10
 64 guideline, the Directive 2008/50/EC introduced additional objectives with respect
 65 to PM_{2.5}. Although various abatement measures have been implemented to reduce
 66 the levels of particulate matter, many European countries still have problems
 67 adhering to the guidelines; in particular, this concerns the maximum number of
 68 exceedances of the daily limit value for PM10. The heavily populated regions in the
 69 north-west of Europe is an example where problematic “hot spots” are found in
 70 urbanised and industrialised agglomerations.

In addition to the strength and location of local, regional and continental 71
 emission sources, levels and chemical composition of ambient PM depend on 72
 climatology, trajectories, rain scavenging potential, recirculation of air masses, 73
 dispersive atmospheric conditions and geography (proximity to coast or arid 74
 zones, topography, soil cover). These factors largely differ over Europe. Reduction 75
 measures in one region may therefore not be optimal for other regions. In the design 76
 of a meaningful abatement strategy, one needs therefore to take into account the 77
 changing characteristics of PM, or more specifically, one should assess which 78
 anthropogenic and natural constituents build up the particulate matter, to what 79
 extent they contribute to the total mass and where they come from. 80

To answer these questions, we elaborated three PM data sets bearing chemical 81
 information that recently became available in the Netherlands, Germany and 82
 Belgium. In addition, a first-order quantitative estimate is given of the ratio between 83
 natural and anthropogenic PM10 mass; this ratio defines the “playing field” of 84
 policy-decision makers. To end, a modelling exercise is described comparing the 85
 major emission sources for north-western Europe (here defined as the three 86
 abovementioned countries) with those of the Iberian Peninsula. 87

2 Concentrations and Chemical Composition at Urban and Rural Sites 88 and Rural Sites 89

2.1 Data Sets 90

During the last decade, a considerable number of studies have focussed on the 91
 speciation of PM in different regions of Europe (e.g. [2–7, 29]). Recently, dedicated 92
 measurement campaigns were carried out in north-western Europe: “CHEMKAR” 93
 (Belgium) by the Flemish Environmental Agency [8], “BOP” in the Netherlands 94
 within the framework of the Netherlands Research Programme on Particulate 95
 Matter [9] and in North Rhine-Westphalia IUTA (Germany). 96

The respective data sets are used here to illustrate the general chemistry of PM10 97
 in north-western Europe. Always, urban and rural sites have been compared. Some 98
 data features are given in Table 1. The components of interest are sulphate, nitrate, 99
 ammonium, elemental carbon, organic carbon, sodium, chloride and elements. 100

2.2 Handling 101

Chemical analyses of PM samples usually provide a major part of the total 102
 particulate mass collected on a filter. Certain tracers or combination of tracers are 103
 used to estimate the contributions from specific sources like sea salt or mineral dust. 104
 In order to make a sound comparison between the three sets, contributions were (re) 105

t1.1 **Table 1** Data sets

t1.2	Country	Name and type of site	Mass fractions	Period
t1.3	Belgium (CHEMKAR)	Zelzate (ub), Borgerhout (ub) Houtem(rb), Aarschot (rb)	PM10	September 2006– September 2007
t1.4	The Netherlands (BOP)	Schiedam (ub), Hellendoorn (rb)	PM10, PM2.5, PM10-2.5	January–August 2008
t1.5	Germany (IUTA/LANUV)	Styrum (ub), Eiffel (rb)	PM10	April–September 2008

t1.6 *ub* urban background, *rb* rural background

106 calculated using the same algorithms. The presence of *secondary inorganic aerosol*
 107 (SIA) is calculated as the sum of NO₃, SO₄ and NH₄ and results from direct
 108 measurements. Sulphate concentrations are corrected for a small amount of sea salt.

109 Carbonaceous compounds in PM contain other elements (e.g. oxygen)
 110 augmenting the organic mass. Organic matter (OM) concentrations are usually
 111 calculated from organic carbon, but the conversion factor remains rather uncertain.
 112 Factors vary between 1.2 and 2 and probably vary between lower values near
 113 sources and higher values after processing in aged air masses. Here, a factor of
 114 1.4 is used which seems most common in literature. Elemental carbon (EC) can be
 115 measured straightforward. In the case of sea salt (SS), there are two tracers: sodium
 116 and chloride. Several algorithms are in practice; one of them calculates the SS part
 117 from both Na and Cl. However, in the case of chloride, reactions with HNO₃ may
 118 occur in the atmosphere as well as on the filter thereby releasing HCl (under the
 119 formation of NaNO₃). In addition, the presence of chloride may suffer from the
 120 evaporation of NH₄Cl (from quartz filters). For these reasons, sodium is selected as
 121 the sole tracer: $SS = 3.26 * Na$ (the factor follows from the composition of sea
 122 water).

123 Various algorithms are also in use to estimate the contribution of mineral dust
 124 (MD). With MD is meant all fugitive windblown and mechanically resuspended
 125 dust with a composition comparable to the earth's crust. Since chemical analyses of
 126 PM samples measure elements directly, the approach here is to sum over those
 127 elements known to be present in the earth's crust: Al, Si, CO₃, Ca, Fe, K, Mn, Ti
 128 and P [10]. Weights were first recalculated to correct for their oxidised form (e.g. Si
 129 is usually present as SiO₂). MD is a parameter difficult to estimate. The use of other
 130 algorithms in the estimation of MD results in different values, e.g. the one
 131 formulated by Denier van der Gon et al. [11]. Also, local anthropogenic sources
 132 may contribute (e.g. metallurgical industry).

133 Finally, the concentrations of all constituents were summated and compared with
 134 the gravimetrically measured mass to establish the unaccounted mass denoted
 135 unknown. The assumption here is that the various data sets accurately describe the
 136 PM characteristics. The filtration devices employed at the sites were all equivalent to
 137 the reference method. However, corresponding studies use different procedures with
 138 respect to filter handling, data treatment and selection, analytical techniques, etc. In
 139 addition, temporal variation, local site characteristics, artefacts like volatilisation
 140 and particle-bound water as well as varying distances from major sources will affect
 141 results in different ways. This will affect the absolute concentrations that have been

measured. Putaud et al. [2] extensively describe the accuracy of the analytical techniques common in Europe. While ion chromatography (SIA) performs well (<10%), an accurate determination of EC, OC and MD remains a challenge. EC concentrations by various techniques differ by a factor of 4, and OC by 30%. The uncertainty in the determination of mineral dust amounts can reach 100% for reasons mentioned above.

Only PM10 is discussed as data on PM2.5 are much less available. In our region, the average mass contribution of PM_{2.5} to PM10 is about 60–70%, and the relative distribution of the different chemical parts in PM2.5 usually resembles that of PM10. All components are present in both the fine and coarse fraction. Whereas SIA, EC and OM dominate more in the fine fraction, SS and MD contribute more to the coarse mode.

2.3 Chemical Composition

Figure 1 shows the chemical distributions for the urban and regional background sites in the three PM10 data sets selected here. Common characteristics can be observed: always, the major constituent is the SIA, followed by the carbon-containing components (EC+OM). Smaller, but non-negligible, contributions arise from MD and SS. At least 81% of the particulate mass was explained in the mass balances. The highest closure was seen at the urban background site Borgerhout (87%) which seems due to relatively a high amount of carbonaceous material. Relatively, there is more SIA present at the rural sites: 42–44% versus 34–41% at urban sites. However, differences between urban and rural sites are not very large stressing the role of SIA in building up background levels [31, 32]. In north-western Europe, agricultural activities (like livestock and soil fertilising) frequently take place yielding high emissions of ammonia in rural areas. Combined with the NO_x emissions from intensified traffic and SO₂ emissions from industry, the formation of ammonium nitrate and ammonium sulphate aerosols is favoured [12].

The sum of EC and OM contributes another 20–27% (at urban sites) and 18–24% (rural) to the PM mass, with OM dominating EC at most sites. Like in the case of SIA, differences between rural and urban sites appear modest which is probably caused by a considerable natural (biogenic) input. A study by ten Brink et al. [13] on the presence of ¹⁴C in PM filter samples revealed that at least 64% of the organic carbon measured at an urban Dutch site was contemporary (i.e. emissions from biogenic material and biomass wood combustion).

A gradient for sea salt is observed as expected. Near the North Sea (Houtem (rural background), Schiedam (urban background)), the marine contribution can be as high as 16–18%. Further inland, some 6–10% is measured. In Germany, it declines to some 4%. On average, the sea-salt contribution in this region is a substantial 10% and is due to the dominance of transport of clean marine air from the West diluting anthropogenic emissions onshore and transporting the pollution further eastward over the European continent.

Urban sites

Rural sites

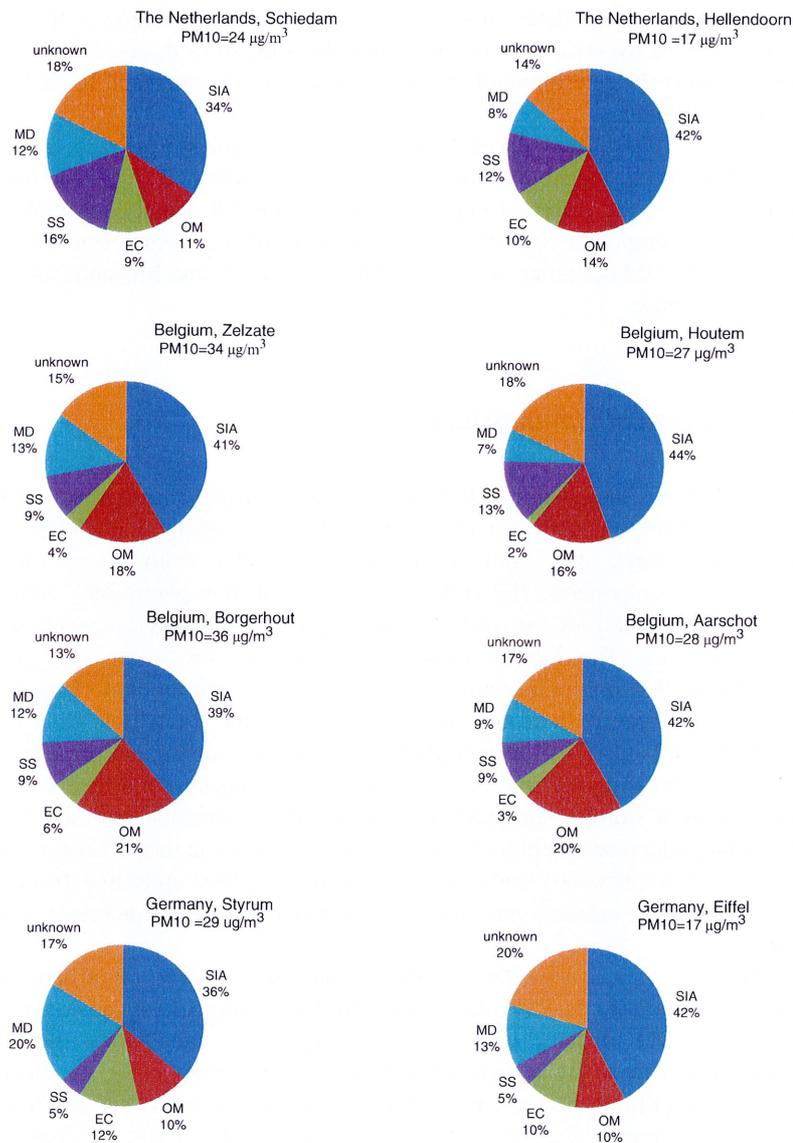


Fig. 1 Chemical distributions for the urban and regional background sites in the PM10 data sets as derived from BOP (the Netherlands), CHEMKAR (Belgium) and IUTA/LANUV (Germany)

184 The fourth constituent, mineral dust, appears comparable in Belgium and the
 185 Netherlands: 12–13% at urban sites and 7–9% at rural sites. A deviant level of MD
 186 is observed at the both German sites (20% and 13%, respectively) and is attributed
 187 to industrial emissions (steel industry) in this region.

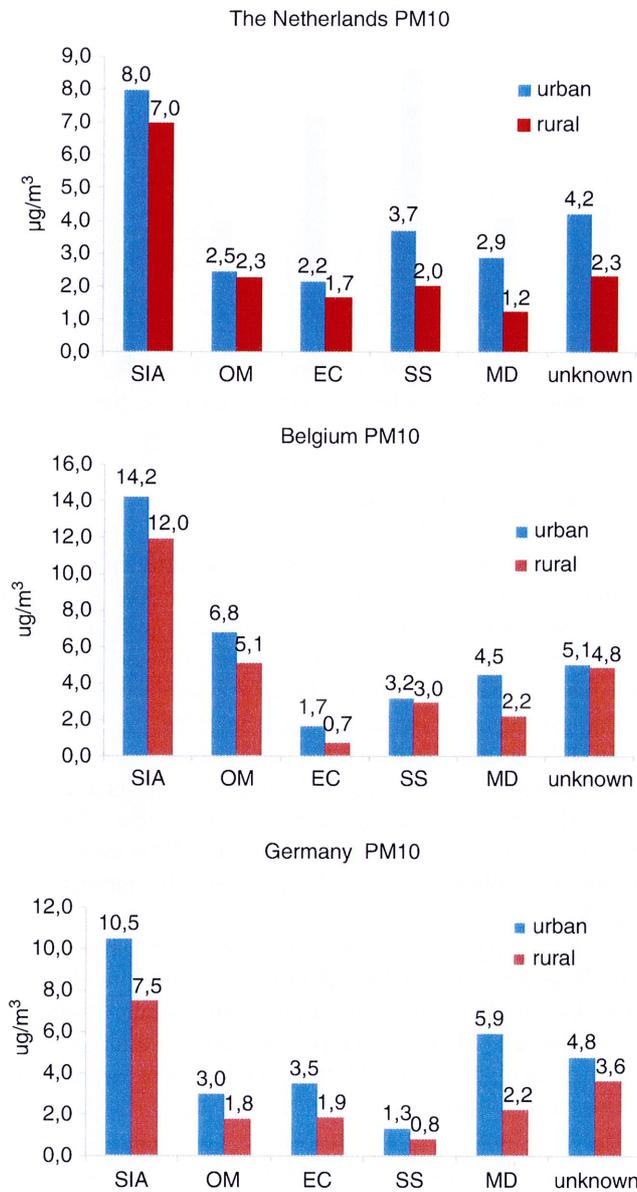


Fig. 2 Chemical distributions for the urban and regional background sites in the PM10 data sets as derived from BOP (the Netherlands), CHEMKAR (Belgium) and IUTA/LANUV (Germany)

2.4 The Urban Increment

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In Fig. 2, the absolute concentrations at the urban and rural sites are compared. For the Belgian data set, we averaged over the two urban and two rural sites.

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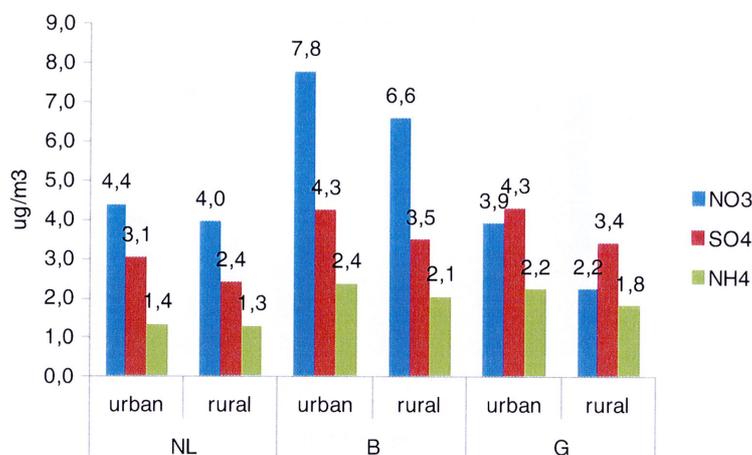


Fig. 3 The urban increment of the SIA components

191 Like in most cities in Europe, a rise in PM10 concentrations is measured when
 192 moving from rural to urban sites. Clearly, a comparison like this depends on the
 193 selection of sites, in particular distance between sites and surroundings affect
 194 results like these. Here, the increase in PM10 is between 7 and 11 $\mu\text{g}/\text{m}^3$. No single
 195 constituent (or emission source) can be held solely “responsible”: all (including the
 196 unknown part) appear higher at the urban sites, but there is no systematic pattern
 197 observed here. In Belgium and Germany, the increment is largely due to more SIA,
 198 OM+EC and MD (between 2 and 4 $\mu\text{g}/\text{m}^3$). In the Dutch data set, however, the
 199 unknown part contributes most. The increase of sea salt at the urban site Schiedam
 200 is due to its location close to the North Sea. The rise of MD is substantial at all sites.
 201 The urban increment observed for SIA systematically returns for each of its
 202 component (Fig. 3).

203 It is seen that the increment of SIA is predominantly caused by nitrate (the
 204 Netherlands and Belgium) and sulphate (Germany), while the change for ammo-
 205 nium is modest. Levels of nitrate and sulphate are usually higher in urban or
 206 industrial areas in Europe [14, 15]. In marine and coastal atmospheres, nitric acid
 207 is converted into particulate nitrate (NaNO_3) through the reaction with sea-salt
 208 particles resulting in the release of HCl: $\text{NaCl} + \text{HNO}_3 \rightarrow \text{NaNO}_3 + \text{HCl}$. In
 209 contrast to NH_4NO_3 , NaNO_3 is a non-volatile compound under atmospheric
 210 conditions; therefore, partitioning of nitric acid into the sea salt is irreversible.
 211 A similar reaction applies for sulphuric acid (and sulphate). Most of the nitrate here
 212 is found in the fine mode as ammonium nitrate (and ammonium sulphate).

213 3 Anthropogenic and Natural Contributions to PM 214 in North-Western Europe

215 Important for air pollution policy in Europe is the contribution to PM10 that is of
 216 anthropogenic origin. It is this fraction that can be targeted by national and
 217 European abatement strategies. Below, a first-order rather pragmatic assessment

is given of the natural versus anthropogenic contributions to PM in north-western Europe. It is based on the prevalence of major constituents in the chemical mass closure while incorporating specifics of the region considered.

Sea spray emissions are the most important natural source of primary sulphate. Applying the sodium-to-sulphate ratio in seawater learns that roughly 5% of the particulate sulphate is of marine origin. Though sulphate may be emitted directly into the atmosphere [17], its major source is the oxidation of sulphur dioxide. In north-western Europe, anthropogenic SO₂ emissions are derived mostly from the combustion of sulphur-containing fuels for power generation and international shipping. In Europe, natural emissions for SO₂ include volcanoes, but given location, height and distance to the Netherlands, their contribution is probably low (i.e. not more than 1% to ground level sulphate). Contributions of other biogenic sources of SO₂ like oxidation of DMS, COS and H₂S are also of minor importance [16]. Wildfire emissions of SO₂ are commonly neglected in studies directed to wild land fire emissions. In the approximation here 5% is used as a conservative estimate. To estimate how much of the nitrate is natural, emissions from soil, biomass burning and lightning should be considered. Studies on NO emissions from soil report emissions between 59 and 190 kton in the EU15 ([17, 30]). Relative to the total inventoried emissions, the central value is 4%. From these emissions, about two-third is attributed to agricultural soils and one-third to forest soils. Soil NO_x emissions largely depend on the nutrient input (through fertilisation or atmospheric deposition) implying that the abovementioned contribution is only partly natural. Lightning depends linearly on the amount of convective precipitation. In Europe, corresponding emissions are estimated to be about 1% (65 kton) of the total inventoried emissions. It mainly takes place between 1 and 5 km altitude and mostly in southern Europe (Friedrich et al. 2008). Wild fires estimates range between 20 and 50 kton (Friedrich et al. 2008; [18]) and occur mostly in countries around the Mediterranean. Given the short life time of NO_x and the rather short transport distance of nitrate, we assume that lightning and wild land fires can be neglected as sources in north-western Europe. In the approximation here, the natural fraction of NO_x emissions and therewith nitrate is taken between 0% and 5%.

Ammonium in aerosols originates from the neutralisation of sulphuric and nitric acid by ammonia. Ammonia is emitted by different sources, most notably animal manure, traffic and application of fertiliser. In general, emissions are for the largest part (80–95%) associated with agricultural activities [19]. Erisman et al. [20] estimated the natural emissions at about 10% of the total emissions in Europe. This percentage includes contributions from wild animals and wetlands. We assume a similar percentage for ammonium in north-western Europe.

The main source of elemental carbon is the (incomplete) combustion of fossil fuels. Wild land fires are occasional sources of vast amounts of carbonaceous particles. Though wild land fires may seem natural, the vast majority of present-day fires are due to human behaviour. Hence, elemental carbon is almost exclusively anthropogenic.

Organic matter contains numerous chemical constituents of which only a small fraction has been identified. Organic carbon is released by the incomplete combustion of fuels but in addition originates from farming activities (stables, harvesting)

264 as well as from nature. Anthropogenic combustion sources as well as (small) stable
265 emissions have been inventoried. Half of the observed concentrations of OC
266 [21, 22] can be explained. Hence, a significant (unknown) contribution is from
267 anthropogenic sources like secondary formation, wildfires, harvesting, abrasion
268 processes and biological material (fungal spores and plant debris). As mentioned
269 previously, ^{14}C analysis suggests that some 70% of the OC mass in the Netherlands
270 is of living material where biogenic SOA, agriculture and other landscaping
271 activities may have contributed. The complicating factor in the estimation of the
272 natural part of OM is the uncertainty related to its secondary component (oxidation
273 of VOCs yields products with low vapour pressures that may condense on existing
274 aerosol) as the major formation routes are not well known. As a consequence, the
275 ratio of natural to anthropogenic SOA is under debate. It is postulated that biogenic
276 sources are a major contributor to atmospheric SOA (e.g. [22]). Assuming that the
277 unexplained OC using present-day emission inventories is for the largest part SOA,
278 an upper limit of around 50% for natural OM is obtained. As a substantial part of the
279 SOA may very well be anthropogenic, it is postulated that half of the SOA as
280 natural, leading to a lower limit of 25% for natural OM.

281 Sources of mineral dust in total PM₁₀ are wind erosion of bare soils, agricultural
282 land management, resuspension of road dust from paved and unpaved roads, road
283 wear, handling of materials and building and construction activities. Only wind
284 erosion may contribute to the natural fraction. Saharan dust is regularly transported
285 to countries around the Mediterranean Sea. In north-western Europe, dust transport
286 from the Sahara occurs once or twice a year and is therefore not very significant.
287 Korcz et al. [23] and Schaap et al. [24] show that windblown dust at the European
288 continent is a rather small source compared to traffic resuspension and agricultural
289 land management. More importantly, the windblown dust source strength from
290 soils other than arable land is low. Windblown dust emissions are strongly related to
291 anthropogenic changes in surface vegetation cover and are regarded as mostly
292 anthropogenic. Consequently, the total mineral dust concentration in air is expected
293 to be anthropogenic for a large part. In the approximation, 10% is assumed as a
294 conservative estimate for the natural contribution to MD.

295 The emission of sea salt is mainly dependent on wind speed. It is considered the
296 second largest contributor in the global aerosol budget, as a vast area of the earth
297 consists of sea. The aerosols consist mainly of sodium chloride. Other constituents
298 of atmospheric sea salt reflect the composition of sea water (magnesium, sulphate,
299 calcium and potassium). Sea salt is the only pure natural aerosol component.

300 The anthropogenic contribution of the unknown part is by definition unknown.
301 Water accounts to some extent for the unknown fraction. As most of that water may
302 be associated with SIA, it is likely that a significant part of the unknown fraction is
303 anthropogenic. It is assumed that the anthropogenic and natural parts of the
304 unknown fraction resemble those of the defined mass.

305 The natural fraction in the total mass can now be obtained by adding the relative
306 natural mass contributions per constituent. For instance, 10% of PM₁₀ is associated
307 with sea salt adding to 10% of natural PM₁₀ (see Table 2). Note that this fraction
308 represents the source attribution and therewith fresh sea salt as discussed in the

Table 2 Analysis of the natural contribution (%), for all components, and for PM10 as a whole, at the rural background site (Hellendoorn) t2.1

Composition	PM10 (%)	Natural contribution (%)	Rural background PM10 (%)	t2.2
NO ₃	20	0–5	0–1	t2.3
SO ₄	14	5	1	t2.4
NH ₄	8	10	1	t2.5
MD	10	20	2	t2.6
SS	10	100	10	t2.7
EC	6	0	0	t2.8
OM	15	25–50	4–8	t2.9
Sum known			18–23	t2.10
Unknown	15	– ^a	3–3	t2.11
Total			21–26	t2.12

For each constituent, the relative contributions to PM10 are listed as well as the estimated natural contributions. The last column provides the resulting natural contribution, expressed in a percentage of PM10 mass (with a low-high estimate for the natural contribution in NO₃ and OC) t2.13

^aThe natural contribution is assumed to be the same as the total natural percentage of PM mass without the unknown fraction

previous section and would be lower when one reflects the chloride loss in this calculation. Nitrate contributes 20%, of which 0–5% is assumed to be natural resulting in a contribution of 0–1% natural PM10 for the low and high case, respectively. Hence, nitrate contributes very little to the natural fraction. Adding all contributions, the estimated natural fraction of PM10 is between 21% and 26%. Hence, between one-fifth and one-quarter of PM10 is estimated to be of natural origin. The uncertainty in such a simple analysis is quite large. Hence, we rounded all data to the closest interval of a half per cent. As such, the uncertainty in the summation is around 2–3%. It is concluded that the most important natural contributions originate from sea salt (100%) and organic material (with an upper limit of 50%).

4 Modelled Origin of Particulate Matter in the Netherlands and Spain

So far, we have used composition measurements and mass closure studies to interpret PM distributions and origin. Furthermore, a simple analysis on the natural fraction of PM was described. Detailed speciation data sets such as used in this study enable to use more elaborate statistical approaches to identify source origins, such as positive matrix factorisation [25]. Examples of these techniques are given for Germany elsewhere in this book (Quass et al. 2012). However, these methods are only able to distinguish between a limited number of source categories. Furthermore, they are typically not able to provide a source apportionment for secondary components.

331 Complementary to experimental data, a chemical transport model (CTM) can be
332 used to obtain a more detailed source apportionment. CTMs provide calculations of
333 the evolution of the air pollution situation across a region based on emission
334 inventories and atmospheric process descriptions. Here we use the LOTOS-
335 EUROS CTM to investigate the origin of particulate matter in north-western
336 Europe. The LOTOS-EUROS model has been equipped with a module that tracks
337 the contribution of different source sectors throughout a model simulation [26].
338 Hence, for each modelled process, e.g. advection and chemistry, the concentration
339 change is calculated as well as change in source contributions. The module has been
340 used to assess the origin of PM in the Netherlands by Hendriks et al. [27]. Here, we
341 summarise the results for the Netherlands assuming it to be representative for north-
342 western Europe (i.e. Belgium and western Germany) and also provide results for
343 Spain to contrast the two regions.

344 To assess the source contributions to modelled PM₁₀, two simulations were
345 performed. A simulation across Europe at 0.5° longitude × 0.25° latitude (about
346 28 × 28 km) resolution provided the results which were used as boundary
347 conditions for a simulation at a resolution of 0.125° longitude × 0.0625° latitude
348 (7 × 7 km) centred over the Netherlands. The simulations were performed for
349 2007, 2008 and 2009 to average out meteorological variability. Labels were applied
350 to distinguish Dutch and foreign emissions sources specified to SNAP (Selected
351 Nomenclature for sources of Air Pollution) level 1, which uses ten main sectors:

- 352 1. Power generation: combustion in energy and transformation industries
- 353 2. Other combustion: nonindustrial combustion mainly households
- 354 3. Industrial combustion in manufacturing industry
- 355 4. Industrial process emissions
- 356 5. Extraction and distribution of fossil fuels and geothermal energy
- 357 6. Solvent use
- 358 7. Road transport
- 359 8. Other transport: other mobile sources and machinery
- 360 9. Waste treatment and disposal
- 361 10. Agriculture

362 Natural emissions and PM originating from the initial conditions, aloft
363 conditions and PM coming from regions outside the model domain were tracked
364 as well.

365 In Fig. 4, the modelled PM₁₀ distribution is shown for Europe. For the
366 Netherlands, modelled PM₁₀ concentrations range from 13 µg/m³ in the North
367 and 18 µg/m³ in the South to 22 µg/m³ in the densely populated and industrialised
368 western part of the country. Comparison to observations shows that present-day
369 chemistry transport models are not able to fully explain the observed particulate
370 matter mass. LOTOS-EUROS misses about 40% of the measured PM₁₀ mass, of
371 which a large part can be explained. The model underestimates nitrate concen-
372 trations by about 25%, whereas total carbon concentrations are underestimated by
373 about 60%. The latter is largely attributed to organic matter and corresponds to up
374 to 4–5 µg/m³ of OM. The reason for the underestimation of organic carbon is that

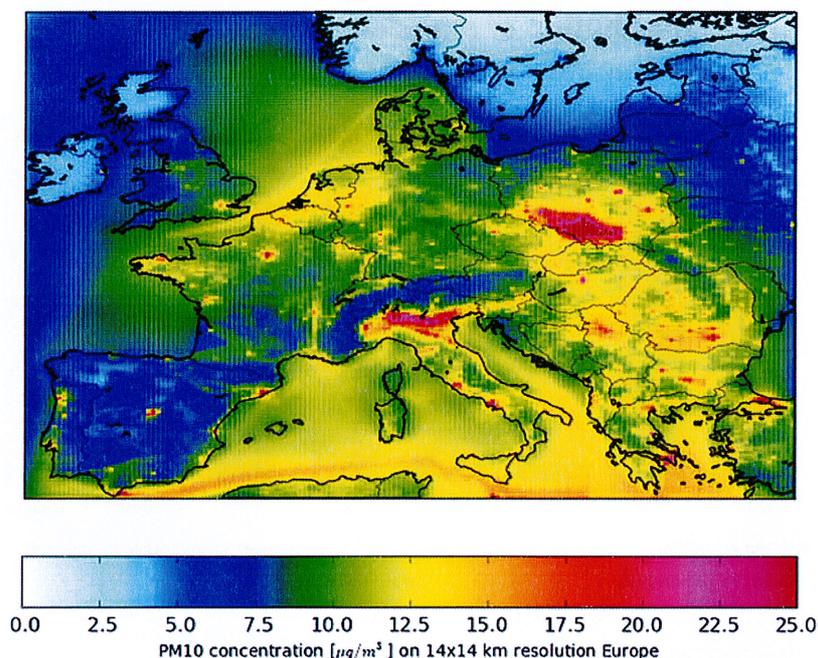


Fig. 4 Modelled distribution of PM10 across Europe for 2007–2009 excluding mineral dust

the model does not include a relevant process description. The uncertainties in the 375
 process description including secondary organic aerosol formation and the semi- 376
 volatile nature of OM are so large that they are not considered robust enough to 377
 incorporate in a source apportionment study. Model to observation comparison 378
 shows no significant biases for sulphate, ammonium and sea salt. Hence, the source 379
 apportionment presented here covers about 60% of the observed PM mass. 380

The source apportionment is performed for each component separately. Figure 5 381
 shows the source attribution per sector for the most important PM components 382
 averaged across the Netherlands. Some components are dominated by a few sectors. 383
 Agriculture is by far the most important source of ammonium, causing over 90% of 384
 the emissions and concentration of this substance in the Netherlands. The mineral 385
 dust concentration in the Netherlands originates for about 25% from outside the 386
 model domain which is mainly associated with a few desert dust episodes. The 387
 remaining mineral dust is equally divided between agriculture and road transport. 388
 The unspecified primary particulate mass is dominated by industrial process 389
 emissions. Nitrate, sulphate and EC concentrations originate mainly from sectors 390
 in which fuel combustion is important (e.g. transport, industrial combustion and 391
 power generation). For the other components, the sector origin is more diffuse. 392

Summing all separate contributions allows to assess the origin of the modelled 393
 total mass. The most important contributions to total PM10 mass in this region are 394
 associated with agriculture, on-road and off-road transport and natural sources. 395
 Together these explain about 75% of the modelled mass. Secondary contributions 396

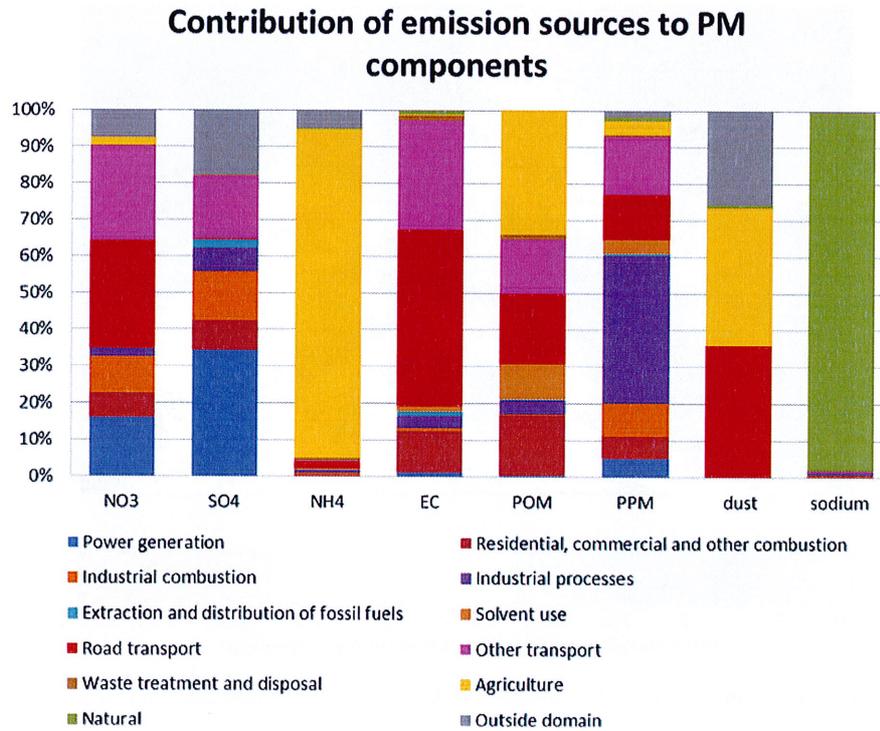


Fig. 5 Annual average origin of modelled PM₁₀ components in the Netherlands [27]

397 are derived from power generation, industrial processes and combustion as well as
 398 households. Waste treatment, solvent use and extraction of fossil fuels do not
 399 contribute significantly. Of the modelled part, 70–80% of PM₁₀ over the
 400 Netherlands is anthropogenic, which is in agreement with the analysis described
 401 in the previous section.

402 To investigate the differences in source contributions between peak episodes and
 403 periods with lower modelled PM concentrations, all days were categorised based on
 404 the average modelled concentration of PM₁₀. The source attribution as function of
 405 PM₁₀ concentration in the Netherlands is shown in Fig. 6. The natural contribution
 406 is highest when the total modelled PM concentration is low. Low concentrations are
 407 associated with westerly winds, resulting in transport of sea salt from the North Sea
 408 and Atlantic Ocean to the Netherlands. High PM concentrations occur mainly with
 409 easterly winds and/or stable stagnant conditions, during which the influx of sea salt
 410 is much smaller. The increase in concentration going from low to high PM levels is
 411 proportional for most sectors, except for agriculture and transport, which become
 412 more important mainly due to the more than proportional rise in ammonium nitrate
 413 concentrations. In the high concentration range also the impact of a few desert dust
 414 episodes is visible.

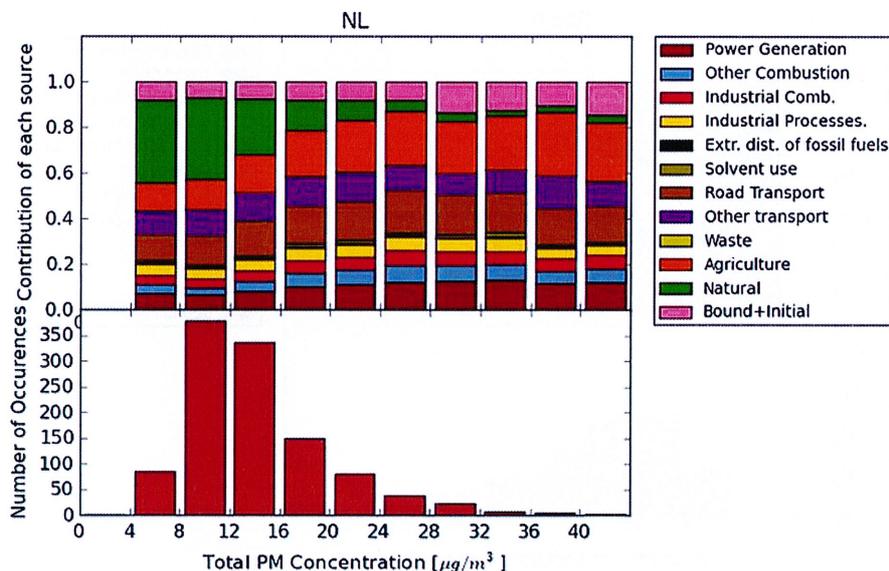


Fig. 6 Modelled source attribution on a sectorial basis for the Netherlands as function of total modelled PM10 mass. For each concentration bin, the number of occurrences is given

To contrast the situation in north-western Europe, we also present results for 415
 Spain. Before addressing the source attribution, we need to highlight an important 416
 difference between the two regions. In north-western Europe, the population 417
 density is generally high, and cities are located close to each other. In Spain, this 418
 is not the case. Major cities with high PM10 concentrations are located far from 419
 each other, and away from the coast population density is very low. Hence, large 420
 differences in concentrations are present between the rural background and urban 421
 concentration levels. 422

Figure 7 presents the source attribution as function of modelled PM10 concentra- 423
 tion averaged across the whole Spanish mainland. Hence, the apportionment is 424
 dominated by the rural areas. This feature also explains the relatively low modelled 425
 concentrations, also in comparison to north-western Europe. Note that the emissions 426
 from the ocean are depicted as natural, whereas those of dust are classified as 427
 boundary. This is due to the fact that a global model simulation incorporating desert 428
 dust is used to provide the influx at the model domain boundaries. Whereas sea-salt 429
 concentration decreases with PM in Spain, the impact of desert dust on PM episodes 430
 is clearly recognisable and, for obvious reasons (Saharan desert sand), much larger 431
 than in north-western Europe. Summarised, the natural sources (sea salt and desert 432
 dust) contribute about half of the modelled PM10 concentrations across the whole of 433
 Spain. Anthropogenic sources that contribute significantly are similar to those in 434
 north-western Europe and comprise agriculture, transport and industrial combustion. 435
 Zooming into large urban agglomerations such as Madrid and Barcelona, the impor- 436
 tance of anthropogenic sources is significantly larger than for the country as a whole 437
 and cause regional maxima modelled PM10 (Fig. 4). It is especially the transport 438
 sector that significantly gains importance. 439

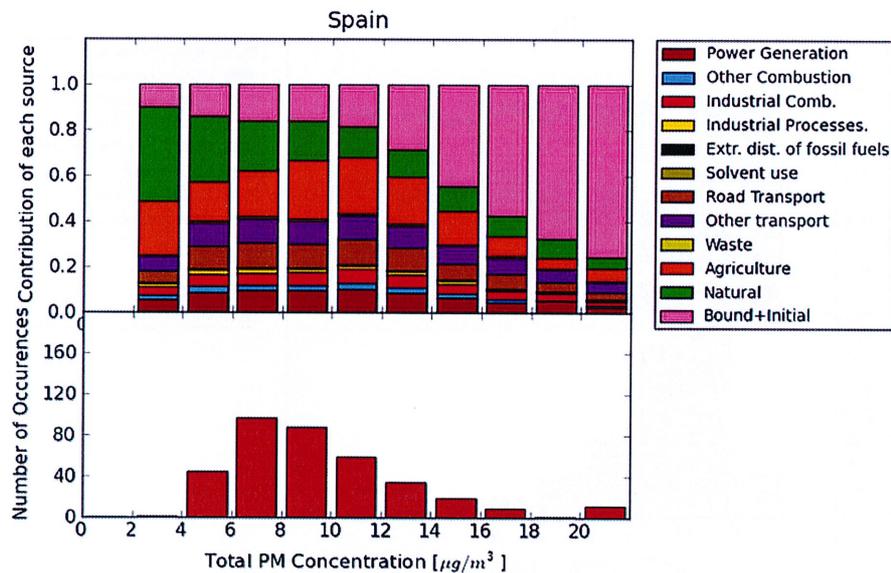


Fig. 7 Modelled source attribution on a sectorial basis for the Spain as function of total modelled PM10 mass. For each concentration bin, the number of occurrences is given. Note that desert dust is incorporated as boundary conditions in the simulations, explaining the large contribution of boundary conditions for Spain

440 5 Concluding Remarks

441 The chemical composition of PM10 on various measurement sites in the
 442 Netherlands, Germany and Belgium shows a considerable conformity. Always,
 443 SIA is the major constituent ($\pm 40\%$) followed by the carbonaceous compounds
 444 ($\pm 25\%$). Contributions of sea salt and mineral dust vary between 10% and 15%
 445 depending on location (distance to the North Sea) or presence of local sources. The
 446 unidentified mass is only in the order of 15% showing that the composition of PM10
 447 in the region is rather well known.

448 PM10 concentrations are systematically higher at urban sites. Roughly, every
 449 constituent in PM10 appears higher in the urban area. The reduced dispersion in
 450 urban areas and the presence of dominating (anthropogenic) sources are the main
 451 reasons. However, the locations and distance between the rural and urban site may
 452 also have influenced the analysis. For instance, the higher urban concentrations of
 453 sea salt are induced by a closer proximity to the coast, though a small gradient in
 454 salt may be explained by the resuspension of road salt in winter. Elementary carbon
 455 in cities primarily originates from diesel emissions. The organic mass is a very
 456 complex group with anthropogenic and natural sources. Although Robinson et al.
 457 [28] showed that photo-oxidation of diesel emissions rapidly generates organic
 458 aerosol ten Brink et al. [13], indicated that only one-third of the OC in a Dutch city
 459 was due to fossil fuel combustion. Hence, the origin of OM remains unclear.

Mineral dust sources in urban areas include road dust resuspension and demolition 460
 and construction activities. There is no apparent reason why the unknown part 461
 should also be higher or lower at urban or rural sites. A possible cause may be the 462
 amount of water attached to SIA which appears increased. Hygroscopic salts on 463
 particles, like ammonium nitrate and ammonium sulphate in the fine fraction, and 464
 sodium nitrate and sodium sulphate in the coarse fraction attract water erroneously, 465
 increasing the PM mass. 466

The reason why SIA is higher in urban areas is less obvious as these are 467
 secondary aerosols. The observed increment is predominantly caused by more 468
 nitrate and sulphate. The reaction of nitric acid and sulphuric acid with the sea- 469
 salt aerosol in a marine urbanised environment follows an irreversible reaction 470
 scheme. In essence, the chloride depletion stabilises part of the nitrate and sulphate 471
 in the coarse mode and may partly explain part of the observed increment. How- 472
 ever, it also raises the question how to assign the coarse mode nitrate in the mass 473
 closure. The sea salt and nitrate contributions cannot simply be added any more as 474
 nitrate replaces chloride. Reduction of NO_x emissions may cause a reduction of 475
 coarse mode nitrate, which is partly compensated by the fact that chloride is not lost 476
 anymore. A reduction would yield a net result of $((\text{NO}_3\text{-Cl})/\text{NO}_3 = (62-35)/62=)$ 477
 27/62 times the nitrate reduction (where the numbers are molar weights of the 478
 respective components), and this factor could be used to scale back the coarse 479
 nitrate fraction in the chemical mass balance. A similar reasoning may be valid for 480
 the anthropogenic sulphate in the coarse fraction. Corrections like these are uncom- 481
 mon in current mass closure studies, and consequences will have to be explored in 482
 more detail. 483

Important for the national and European air pollution policy is the question how 484
 much of the measured particulate matter is of anthropogenic origin. It is this 485
 fraction that can be targeted by national and European abatement strategies. A 486
 pragmatic assessment of the natural versus anthropogenic contributions to PM was 487
 given here. The estimation is that between 20% and 25% of PM10 is of natural 488
 origin for countries like Germany, Belgium and the Netherlands. Hence, the 489
 majority of PM in the north-western European region is of anthropogenic origin. 490
 The uncertainty in such an analysis is considerable, and the result should be taken as 491
 indicative. 492

A CTM was used to obtain a more detailed source apportionment for the 493
 Netherlands. The model explains about 60% of the observed PM10 mass concen- 494
 tration. Application of a dedicated source apportionment module showed that the 495
 origin of the individual species may differ considerably. The most important 496
 contributions to total PM10 mass in north-western Europe are associated with 497
 agriculture, on-road and off-road transport as well as natural sources (sea salt). 498
 Together these explain about 75% of the modelled mass. Secondary contributions 499
 are derived from power generation, industrial processes and combustion as well as 500
 households. Of the modelled part, 70–80% of PM10 over the Netherlands is 501
 anthropogenic. The increase in source contribution going from low to high PM 502
 levels is proportional for most sectors, except for agriculture and transport, which 503
 become more important mainly due to the more than proportional rise in ammo- 504
 nium nitrate concentrations. Sea-salt concentrations decline with rising PM10. 505

506 Whereas sea-salt concentrations also decrease with rising PM in Spain, the
 507 impact of Saharan dust on PM episodes is clearly recognisable and much larger
 508 than in north-western Europe. The natural sources (sea salt and desert dust)
 509 contribute about half of the modelled PM10 concentrations across the whole of
 510 Spain, according to our modelling exercise. Anthropogenic sources that contribute
 511 significantly are similar to those in north-western Europe.

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